Tracking the Geochemical Evolution of Coal Mine Drainage with Radiogenic Isotopes

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Acid mine drainage (AMD) is formed by the atmospheric oxidation of pyrite, a common iron sulfide mineral associated with coal seams. This weathering process usually results in acidic, iron- and sulfate-rich waters that precipitate metal oxides into their receiving streams. Polluted drainage from abandoned coal mines degrades more than 12,000 km of streams and rivers in the U.S.A. The economic burden of discharge remediation has motivated mining companies and regulatory agencies to develop predictive models for mine discharges. This has been used successfully to manipulate surface mine drainage, where overburden rocks and chemical reactions are relatively simple to characterize. New methods are needed to determine and quantify the effect that coal overburden has on the production and composition of deep mine discharges.

While coal mine discharges are often highly acidic (pH < 3), some are net alkaline with a pH of 6 to 7 (Weaver et al., 1997; Rose and Cravotta, 1998). Archival data indicate that some discharges became net alkaline within several years, while others remain highly acidic even thirty years after mining has stopped (Weaver et al., 1997; Brady et al., 1998). The pH of mine waters is the result of both acidity and alkalinity producing reactions. Most mine drainage remediation efforts focus on reducing acidity by controlling bacteria, pH, oxygen, temperature, and the weathering rate of pyrite. Understanding natural alkalinity production offers alternative approaches for neutralizing AMD and has implications for predictive models, mining regulations, mine discharge remediation, and resource recovery.

We have begun to apply strontium isotopes to the analysis of deep bituminous coal mine discharges and related overburden rocks to (1) assess the reliability of this method as a predictor of subsurface geochemistry, and (2) to determine the nature and relative contributions of subsurface processes involved in the generation of natural alkalinity in deep discharges. The strontium isotopic composition of mine waters should reflect the character of the rocks and waters with which they have interacted (Hunt et al., 1998). If the various sources contributing to the ⁸⁷Sr/⁸⁶Sr of coal mine discharges are isotopically distinct, Sr isotopes could trace the reactions involved in the geochemical evolution of coal mine drainage. These reactions likely include dissolution of calcareous rocks, silicate mineral weathering, and cation exchange (Rose and Cravotta, 1998; Younger, 1998).

The depositional environment of the Late Pennsylvanian (~290 My old) sedimentary rocks of the northern Appalachian region varied from freshwater to marine. The Freeport Coal of the Allegheny Group and the overlying Pittsburgh Coal of the Monongahela Group are capped by overburden limestones and shales that formed in a freshwater environment. The overburden strata of the Allegheny Group Clarion and Kittanning coals are of marine and brackish water

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origin, respectively. The pH of the discharges ranges from 2.8 to 6.6, and alkalinity (as $CaCO_3$) from 0 to 439 ppm. Iron (Fe) and manganese (Mn) content is highest in the Allegheny Group Clarion coal discharges (48-385 ppm Fe; 17 to 91 ppm Mn). The Monongahela Group Pittsburgh coal discharges have 1-78 ppm Fe and < 3 ppm Mn. We found that the concentration of dissolved Al in the mine discharges with pH > 5 is <1 ppm, and \leq 0.3 ppm in discharges with pH \geq 5.8. Typical AMD generally plots near the upper apex of a Piper plot; but the Pittsburgh coal discharges show a trend of increasing alkalinity and sodium (Fig. 1). In the Irwin basin (Pittsburgh coal) discharges, alkalinity, pH, and concentration of Ca^{+2} and Na^{+} increase from north to south, most likely as a result of calcite dissolution and cation exchange (Weaver et al., 1997; Winters et al., 1999). This is reflected in higher concentrations of dissolved aluminum and

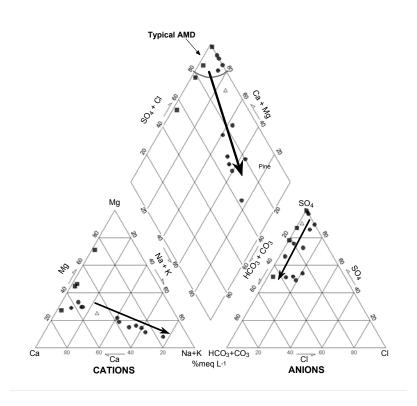


Figure 1. Piper plot showing cation and anion trends for northern Appalachian coal mine discharges. Arrows indicate deviations from "normal" AMD chemistry.

We focused our initial Sr isotope work on the Pittsburgh coal AMD outflows. Acidic and alkaline waters were collected from a series of discharges along the Irwin Basin. Two limestones were collected from the thick and laterally extensive Benwood Formation (Reynolds Capo, 2000). Two silicate rock samples were collected in the Irwin syncline at Upper Guffey site: calcareous shale three feet above the Pittsburgh Coal, and a clay-parting between the upper and lower bench of the Pittsburgh Coal.

The ⁸⁷Sr/⁸⁶Sr composition of freshwater limestone overlying the Pittsburgh coal is <0.711, while the acetic acid and hydrochloric acid soluble fraction of calcareous

clay and shales range from 0.716 to 0.730. The isotopic composition of the mine discharges fall between the silicate and carbonate end member values (Fig. 2), with ⁸⁷Sr/⁸⁶Sr ranging from 0.7114 to 0.7126. With the exception of the Lowber outflow, the isotopic composition of the discharges remained constant at each site from high-flow conditions (March 1999) to low-flow conditions (July 1999). These data demonstrate that a significant portion of the discharge Sr (and by inference, Ca) is derived from the clay and shale units, rather than from the relatively soluble and Sr-rich limestone.

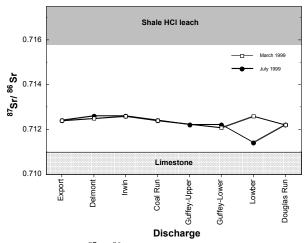


Figure 2. ⁸⁷Sr/⁸⁶Sr variation of coal overburden end members and abandoned mine drainage from the Pittsburgh coal seam.

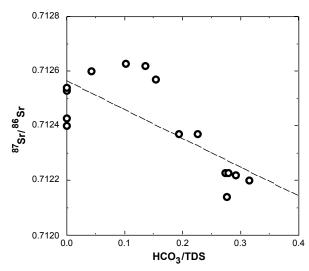


Figure 3. Variation of abandoned mine drainage ⁸⁷Sr/⁸⁶Sr ratios with bicarbonate (normalized to total dissolved solid content).

Our initial data suggest a negative correlation between 87 Sr/ 86 Sr and bicarbonate ($r^2 = 0.6$; Fig. 3). While preliminary, this suggests that Sr is introduced from the shale/clay silicate source by a process that does not involve generation of bicarbonate ions. One possibility is cation exchange processes in the clays, which could lead to exchange of Sr without generation of bicarbonate. An alternative explanation would be silicate dissolution enhanced by oxidation of sulfide, with attendant production of H^+ . We note that there is a moderate correlation of H^{87} Sr/ H^{86} Sr with both Fe and H^{87} Sr with both Fe and H^{87} Sr

Coal mining can drastically and permanently alter the hydrologic, geochemical biological characteristics of large areas. Our preliminary strontium isotope results are promising and suggest radiogenic isotopes can provide information regarding subsurface geochemical reactions involving overburden and deep waters or brines that could effect the composition of the mine waters draining at the surface. Ongoing work involves a more comprehensive study of Allegheny and Monongahela group coal mine discharges and related overburden rocks. This will help in the development of a quantitative hydrogeologic model that could be used in conjunction with traditional techniques to predict the chemistry of deep mine discharges and assess the feasibility of economic treatment at abandoned sites.

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